

Dec 31 01 05:17P

Jan C. Lipscomb

1-336-882-7626
10030066 031,700-2
JC14 Rec'd PCT/PTO 03 JAN 2002

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER Mueller-40
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 10/030066
INTERNATIONAL APPLICATION NO. PCT/DE00/02163	INTERNATIONAL FILING DATE 6 July 2000	PRIORITY DATE CLAIMED 7 July 1999		
TITLE OF INVENTION Method for Producing Metal Oxides Dispersibles in Organic Solvents [as amended]				
APPLICANT(S) FOR DO/EO/US Frank Michael Bohnen, Katja Siepen, Karen Reitz, and Paul K. Hurlburt				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> has been communicated by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input checked="" type="checkbox"/> is attached hereto. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). <input checked="" type="checkbox"/> have been communicated by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input checked="" type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 				
Items 13 to 20 below concern document(s) or information included:				
<ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail <input checked="" type="checkbox"/> Other items or information: Acknowledgment postcard 				

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/03006	PCT/DE00/02163	Mueller-40

24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$1040.00
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$890.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$740.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$710.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00

CALCULATIONS PTO USE ONLY**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

 20 30

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	48 - 20 =	28	x \$18.00	\$504.00
Independent claims	1 - 3 =	0	x \$84.00	\$0.00

Multiple Dependent Claims (check if applicable). \$280.00**TOTAL OF ABOVE CALCULATIONS =** \$1,674.00

Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

\$0.00

SUBTOTAL = \$1,674.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).

 20 30

+ \$0.00

TOTAL NATIONAL FEE = \$1,674.00Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). \$0.00**TOTAL FEES ENCLOSED =** \$1,674.00

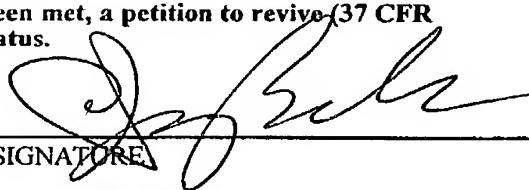
	Amount to be: refunded	\$
	charged	\$

- a. A check in the amount of \$1,674.00 to cover the above fees is enclosed.
- b. Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4345 A duplicate copy of this sheet is enclosed.
- d. Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

C. James Bushman Browning Bushman P.C. 5718 Westheimer, Suite 1800 Houston, Texas 77057-5771 Tel.: (713) 266-5593 Fax: (713) 266-5169
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 SIGNATURE
 C. James Bushman
 NAME
 24,810
 REGISTRATION NUMBER
 113/02
 DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
ACTING AS RECEIVING OFFICE FOR THE PCT

In re Application of:	§	Attorney Docket No.: Muller-40
Frank Michael Bohnen, Katja Siepen, Karen Reitz, and Paul K. Hurlburt	§	
Int'l. Appln. No.:	PCT/DE00/02163	§
Int'l. Filing Date:	6 July 2000	§
Priority Date:	7 July 1999	§
U.S. Serial No.:	To Be Assigned	§
U.S. Filing Date:	Herewith	§
For:	<i>Method for Producing Metal Oxides Dispersibles in Organic Solvents [as amended]</i>	§

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Kindly amend the above-identified application as follows:

In the Specification

On page 1, in lines 1-2, kindly delete the title and insert therefor the following new title:

METHOD FOR PRODUCING METAL OXIDES DISPERSIBLES
IN ORGANIC SOLVENTS

On page 1, after the title and before line 5, please insert the following new heading and subheading:

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

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On page 1, at line 10, please insert the following new subheading:

DESCRIPTION OF THE PRIOR ART

On page 3, at line 33, please insert the following new heading:

SUMMARY OF THE INVENTION

On page 4, at line 8, please insert the following new heading and paragraph:

BRIEF DESCRIPTION OF THE DRAWINGS

The single figure is a graph showing viscosity versus time (days) of an acetone dispersion.

On page 4, at line 8, please insert the following new heading:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the Claims

Please cancel claims 1-17.

Please add the following new claims, 18-38:

NEWLY ADDED CLAIMS

18. (New) A process for preparing modified metal oxides or metal aquoxides that are dispersible in organic solvents comprising:
 - (I) reacting
 - (A) at least metal oxide or metal aquoxide having a crystallite size of 4 to 100 nm, determined by x-ray diffraction on the 021 reflex, and a particle size of 5 to 500 nm, determined by photon correlation spectroscopy in dispersion.

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with

- (B) at least one organic sulfonic acid wherein
- (i) in case the reaction takes place in a mainly aqueous medium or in the absence of a diluent/solvent, the organic sulfonic acid is a mono-, di-, or trialkylbenzene sulfonic acid, wherein the alkyl residue(s) are C₁ to C₆ alkyl residue(s) and wherein the component (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, or
 - (ii) in case the reaction takes place in the presence of an organic aprotic solvent or an organic protic solvent, the organic sulfonic acid comprises at least 14 carbon atoms and at least one aromatic ring, and wherein the components (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, and
- (II) drying the modified metal oxide or metal aquaoxide.

19. **(New)** The process according to claim 18, characterized in that said metal oxide or metal aquoxide contains aluminum.
20. **(New)** The process according to claim 19 wherein said metal oxide or metal aquoxide are selected from the group consisting of aluminas, alumina hydrates, aluminum silicate, Si/Al mixed oxides and mixtures thereof.

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21. **(New)** The process according to claim 20 wherein said alumina hydrates are selected from the group consisting of boehmite, pseudoboehmite and mixtures thereof.
22. **(New)** The process according to any one of claims 18-21, characterized in that the organic sulfonic acid is a toluenesulfonic acid.
23. **(New)** The process according to claim 22 wherein said toluenesulfonic acid is p-toluenesulfonic acid.
24. **(New)** The process according to any one of claims 18-21, characterized in that the organic sulfonic acid has the formula R-SO₃H, wherein R is an alkyl-substituted aromatic hydrocarbon residue with 16 to 24 carbon atoms.
25. **(New)** The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides and the organic sulfonic acid are brought into contact at temperatures from 0 to 140°C.
26. **(New)** The process according to claim 25 wherein the temperature is from 0° to less than 90°C.
27. **(New)** The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides are brought into contact with the organic sulfonic acid for a period of time of from 30 seconds to 7 days.

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28. **(New)** The process according to claim 27 wherein the period of time is from 30 to 90 minutes.
29. **(New)** The process of claim 27 conducted with stirring.
30. **(New)** The process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are dried by spray drying, freeze drying, microwave drying, drying in supercritical solvents, filtration, contact drying, or rotary drum drying.
31. **(New)** The process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are dispersed in organic solvent as dispersions having a solids content of 10 to 35 wt%.
32. **(New)** The process according to claim 31 wherein the solids content is from 20 to 30 weight percent.
33. **(New)** The process according to any one of claims 18-21, characterized in that the metal oxides or metal aquoxides are taken up in an organic solvent and this solvent is exchanged for a second solvent.

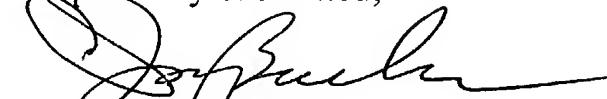
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34. **(New)** The metal oxide or metal aquoxide dispersion comprising a metal oxide or metal aquoxide according to any one of claims 18-21, and a dispersant selected from the group consisting of
 - an aprotic polar organic solvent,
 - a protic, polar organic solvent having at least two carbon atoms,
 - an apolar organic solvent and mixtures thereof.
35. **(New)** The dispersion according to claim 34 wherein the dispersion contains an additive comprising at least one organic polymeric/oligomeric viscosity-adjusting agent.
36. **(New)** The dispersion according to claim 35 wherein the viscosity-adjusting agent is selected from the group consisting of cellulose, a cellulose derivative, a polyacrylate, a polyvinyl alcohol and mixtures thereof.
37. **(New)** The dispersion according to claim 36, characterized in that the dispersant is selected from the group consisting of a solvent-based paint, lacquer, a water-insoluble plastic, and mixtures thereof.

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38. (New) A process according to any one of claims 18-21, characterized in that the modified metal oxides or metal aquoxides are processed into molded articles by extrusion, pelleting, or spherical drop forming processes.

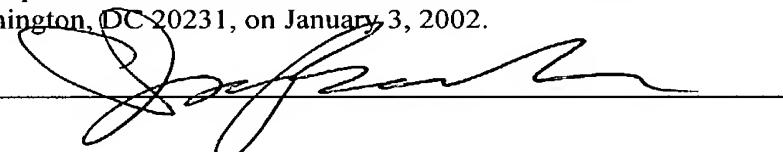
Respectfully submitted,


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CERTIFICATE OF EXPRESS MAILING

I, C. James Bushman, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL715550119US in an envelope addressed to: Box PCT, Assistant Commissioner for Patents, Washington, DC 20231, on January 3, 2002.

By: 

Application as filed
1/PX/

PROCESS FOR THE PREPARATION OF METAL OXIDES THAT ARE DISPERSIBLE IN ORGANIC SOLVENTS

5 This invention relates to a process for preparing metal oxides or metal aquoxides that are dispersible in organic solvents. The invention further relates to metal oxides or metal aquoxides that are modified with organic sulfonic acids and can be prepared by this process.

10 From WO 95/12547 or German patent DE 43 37 643-C1, a process is known for the preparation of nanocrystalline alumina hydrates in boehmitic or pseudoboehmitic form that are dispersible in water. Water-dispersible alumina hydrates can be obtained in this process by hydrolysis of aluminum alkoxides at temperatures from 30°C to 110°C, addition of an acid (monovalent inorganic or organic acids as well as their anhydrides), and subsequent hydrothermal aging. The resultant suspensions are suitable for example for coating materials, such as glass, metal, or plastics, as well as for producing high-strength catalyst supports, pure-phase mixed oxides, or after conversion to the α-form, for producing high-performance abrasives. The water-dispersibility of those alumina hydrates, which are not dispersible in organic solvents, is a disadvantage for certain applications, such as weather-resistant exterior coatings. For certain applications, aluminas that are dispersible in organic solvents but not in water are of interest.

20 30 The aluminas prepared by some of the processes known in the art are dispersible in dilute acids and water, and some of these aluminas are dispersible in short-chain alcohols, such as methanol and ethanol. They are not dispersible in organic aprotic solvents.

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Colloidal alumina solutions in organic solvents are described for example in DE 41 16 522-C2 as well as by R.

- 5 Naß and H. Schmidt ("Formation and Properties of Chelated Aluminum Alkoxides" in H. Haasner, G. Messing, S. Hirano (Eds.) "Ceramic Powder Processing", Deutsche Keramische Gesellschaft, Cologne, 1969). According to said publication, the alumina hydrates obtained by hydrolysis of aluminum alkoxides in an organic solvent and in the presence of a β -diketone compound can occur as colloids in the solvent. However, the colloidal solutions described there are only (meta)stable in the organic solvent at high dilutions. Only for isopropanol as a solvent has it been 15 experimentally proven that the solutions are in fact colloidal ones. Experiments have shown that after removal of the solvent, the colloidal particles prepared by said process cannot be redispersed.
- 20 From AU 200149 a process is known for the preparation of various inorganic oxides and hydroxides that can be dispersed in mineral oils. For this purpose, inorganic oxides or hydroxides are subjected to grinding in a ball mill in the presence of a surfactant and a mineral oil as 25 the carrier fluid. As surfactants, organic sulfonic acids are cited among others. The surfactants are added to the composition in quantities of 0.5 to 3 wt%.

- In US 3,018,172, a process is described for the preparation of aluminum hydroxides that are dispersible in non-polar, high-molecular organic solvents, such as mineral oils. In said process, aluminum alkoxides in a volatile organic solvent are hydrolyzed by contact with an organic sulfonic acid, such as postdodecylbenzenesulfonic acid in

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a viscous organic carrier fluid. After hydrolysis, the volatile organic solvent is removed and an aluminum 5 hydroxide dispersed in a viscous organic carrier fluid, such as xylene, remains.

A similar process is described in US 3,867,296, wherein a high-molecular organic sulfonic acid in a viscous organic 10 carrier fluid is added to alumina hydrates in a volatile organic medium.

US 4,076,638 and US 4,123,231 describe variants of this process. According to US 4,076,638, a carboxylic acid is 15 used in parallel, while the viscous organic carrier fluid is dispensed with. According to US 4,123,231, an aqueous mineral acid is used in addition to the organic sulfonic acid.

20 The processes described in the aforementioned U.S. patents have in common that substantial amounts of organic sulfonic acids must be used compared to the amount of alumina hydrate. In addition, organic solvents are required for the preparation of dispersible alumina.

25 According to AU 200149, mineral oxides are taken up in highly viscous mineral oils having a high solids content and then are dispersed in mineral spirits at high dilutions with a low solids content. However, these are no 30 real colloidal solutions.

After drying, the products obtained by the aforesaid processes are no longer dispersible in organic solvents. It is the object of the present invention to provide dispersible metal oxides/metal aquoxides. It is a further 35

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object of this invention to provide a process for preparing such products, which does not have the disadvantages of the prior art and, for example, does not require organic solvents for their preparation. These problems are solved by the subject matter of the invention.

The subject matter of the present invention is a process for preparing metal oxides or metal aquoxides, especially alumina hydrates that can be dispersed in protic or aprotic organic solvents. Said products can be obtained by reaction of

- (A) one or a plurality of metal oxide(s)/metal aquoxide(s) having a crystallite size of 4 to 100 nm, preferably 6 to 20 nm (determined by x-ray diffraction on the 021 reflex) and a particle size of less than 1,000 nm, preferably 5 to 500 nm, most preferably 20 to 100 nm (determined by photon correlation spectroscopy (PCS) in the suspension prior to drying, for example during the production process)
- (B) one or a plurality of organic sulfonic acid(s), where
 - (i) in case the reaction takes place in a largely aqueous medium or in the absence of a diluent, the organic sulfonic acid is a mono-, di-, or trialkylbenzene sulfonic acid, wherein the alkyl residue(s) is (are) C₁ to C₆ alkyl residues, preferably C₁ to C₄ alkyl residues, and mono-C₁-alkylbenzene sulfonic acids or mono-C₃-alkylbenzene sulfonic acids are preferred, or
 - (ii) in case the reaction takes place in the presence of an organic aprotic solvent or an organic protic solvent, the organic sulfonic

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acid has at least 14 carbon atoms, preferably at least 16, and at least one aromatic ring,

5 wherein the components (A), calculated as metal oxide, and (B) are used at weight ratios from 98:2 to 70:30, preferably from 95:5 to 80:20. Suitable organic protic solvents according to (ii) are for example alcohols, preferably C₂ to C₄ alcohols. Suitable aprotic solvents according to (iii) are for example aromatic hydrocarbons, such as toluene. In case the reaction is carried out in the presence of a largely aqueous medium, it is preferred that the organic sulfonic acid be soluble in the largely 10 aqueous medium.

15

Preferred embodiments are the subject matter of the sub-claims.

20 The solvents used as dispersants according to the invention are:

- (I) aprotic polar organic solvents
- (II) protic polar organic solvents having at least two carbon atoms, or
- 25 (III) nonpolar organic solvents.

Suitable aprotic polar organic solvents (I) include ketones, ethers, and esters, such as acetone, tetrahydrofuran (THF), methyl ethyl ketone, polyol ester, 1,6-hexanedioldiacrylate, and dimethylsulfoxide (DMSO).

Suitable protic polar organic, optionally high-molecular, solvents (II) having at least two carbon atoms include alcohols, polyethers (with at least one free hydroxy group), hydroxylalkyl ethers, and hydroxylalkyl ketones, or carboxylic acids. Suitable alcohols include for example

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ethyleneglycol, C₂ to C₈ mono- or dihydroxy alcohols, such as propanols, butanols, pentanols, and hexanols.

5

Suitable nonpolar organic solvents (III) are for example toluene and chlorobenzene.

The dispersible metal oxides or metal aquoxides obtainable by the process of the invention are powders that can be dispersed in the aforementioned solvents up to a solids content of 35 wt%. The particle size of the dispersed alumina hydrates is preferably from 20 to 1,000 nm (determined by PCS).

15

In a preferred embodiment of the present invention, the metal oxides or metal aquoxides, especially amorphous or nanocrystalline alumina hydrates (with crystallite sizes of up to 100 nm, measured on the 021 reflex, and grain sizes between 0.2 µm and 90 µm with particle sizes of 20 to 1,000 nm in the suspension) are mixed and stirred with 0.2 to 2 grams of *p*-toluenesulfonic acid monohydrate per gram of alumina or metal oxide or metal aquoxide, in each case calculated as metal oxide, at temperatures between 0 and 140°C for a period from 30 to 180 minutes, and are dried by spray drying, freeze drying, drying in supercritical solvents, filtration, or rotary drum drying. The resultant powder retains little water dispersibility (< 30 wt%) and is characterized by a very narrow grain size distribution. The powder can be easily dispersed in the aforementioned organic solvents with particle sizes from 10 to 1,000 nm, preferably from 10 to 500 nm (measured in the suspension).

Part of the suspensions obtained in this way are translucent. They produce transparent coatings, for example on

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films/foils, glass, or similar surfaces. As a result of their dispersibility in organic solvents, the aluminas modified in this way are suitable for incorporation into various water-insoluble polymers or lacquers/paints.

Most cf the suspensions prepared in this way are opaque. They are characterized by excellent sedimentation and 10 centrifugation stabilities. Hence, they are genuine colloidal solutions. Another peculiarity is their redispersibility, especially after drying, in organic solvents, and the possibility of making stable suspensions with a high solids content (> 20 wt%). Surprisingly, the 15 metal oxides/metal oxide hydrates obtained by the process of the present invention remain dispersible in the aforementioned dispersants (I) to (III), even after drying and, optionally, after finishing and/or storage.

20 In contrast to suspensions of alumina hydrates in aqueous systems, the viscosity increases only slightly at the beginning and then remains constant after one day (see Fig. 1/1). No sedimentation occurs, even not after several weeks. Owing to these properties, the p-toluenesulfonic 25 acid-modified alumina hydrate of the invention is particularly easy to process and is most appropriate for making transparent coatings. Furthermore, it is useful as a filler in hydrophobic materials, such as PVC or lacquers/paints based on organic solvents.

30 **Dispersing Procedure**

Into a beaker, there were placed 18 grams of solvent and, while stirring vigorously, 2 grams of modified alumina 35 hydrate were added in portions into the vortex within 1 to 5 minutes. The mixture was stirred for additional 10

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minutes. The resultant suspension had a solids content of 10 wt%. No sedimentation will occur with readily dispersible products. Dispersibility was determined by centrifugation of the suspension at 2,000 rpm (10 min), drying (at 120 °C), and weighing of the precipitate.

By the term 'dispersible metal oxides/metal aquoxides' employed herein especially those products are characterized which, when following the procedure described hereinbefore, remain in a dispersed state at >/= 95 wt% or >/= 98 wt%.

15 Example 1

20 grams of water-dispersible nanocrystalline alumina hydrate (crystallite size measured on the 120 reflex: 8-12 nm) (CONDEA product Disperal™ S), corresponding to 20 14.4 grams of Al₂O₃, were dispersed in a solution of 4 grams of p-toluenesulfonic acid in 180 grams of demineralized water and heated to 90°C for 30 minutes with stirring, thereby adjusting the pH-value to 1.5 and moderately thickening the suspension. After cooling, the suspension was spray dried (inlet temperature 240 to 270°C, outlet temperature < 110 °C). A white odorless powder was obtained the properties and dispersibility of which are shown in Table 2 and Tables 1 and 4, respectively.

30 Example 2 (PTSA-Modified Silica Alumina)

Batch: 180 grams of demineralized water
4 grams of p-toluenesulfonic acid (PTSA)
20 grams of Siral™ 30 D

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A suspension of 20 grams of Siral™ 30 D was prepared in a solution of 4 grams of *p*-toluenesulfonic acid in 180 5 grams of demineralized water. The resultant yellowish sol-like suspension was spray dried. The C-value after drying was 8.61%. The powder was redispersible at 99% in water and ethanol. After solvent exchange, it was redispersible in hexanol and ethylene glycol, too.

10

Example 3

4 grams of postdodecylbenzenesulfonic acid (Marlon™ AS-3) were dissolved in 180 grams of toluene. 20 grams of 15 Disperal™ S were added. The mixture was stirred at 80°C for 30 minutes. The resultant yellowish sol with a solids content of approx. 10% contained aluminum oxide particles having a size of about 195 nm (measured by PCS). The sol was at 97.3% stable to centrifugation (10 minutes at 20 2,000 rpm). After removal of the solvent at 40°C/77 mbar, a yellowish crystalline powder was obtained which was redispersible in toluene, tetrahydrofuran (THF), butanol, methyl-*tert*-butyl ether (MTBE), and trichloromethane. In chlorobenzene, a translucent suspension can be obtained, 25 which is not stable to centrifugation, however. The powder is 100% hydrophobic, i.e., dispersibility in water was reduced to 0% by reaction with Marlon™ AS-3. The organosols are characterized by their long-term stability to agglomeration. No increase in viscosity was observed 30 after several days. The dispersibility of the powder is shown in Table 3.

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Table 1 Dispersibility in Various Organic Solvents

Solvent	Dispersibility (up to 10 wt% solids)	Particle Size [nm]	Transmission (0.1% solids) [%]	Remarks	Centrifugation Stability (2,000 rpm/10 min) [%]
Acetone	Yes (opaque)	80	60.8%	With 20% solids: thixotropic	84.2%
Ethanol	Yes	100	84.5%	-	99.0%
i-Propanol	Yes (limited)	-			Not determined
n-Butanol	Yes (opaque)	97			99.5%
Hexanol	Yes	335	65.8%	Thixotropic	84.6%
Ethyleneglycol	Yes (opaque)				
THF	Yes (opaque)	121			96.5%
DMSO	Yes (opaque)	104			95.0%
Chlorobenzene	By solvent exchange *	400		Low viscosity	99.5%
Dichloromethane	No	-			-
Toluene	By solvent exchange *	PCS not possible		Gelatinized	Not determined
1,6-Hexamethylene- diacrylate	By solvent exchange *	-		Polymerized in UV	Not determined

5

- * At first dispersion in acetone, then addition of equal amounts of solvent (here: chlorobenzene), followed by displacement of the acetone by stirring with heating to 40 °C.

10

Table 2 Physical Characteristics of the Powder

		9.1 wt% PTSA	16.8 wt% PTSA
Specific surface area (BET) (activated for 3 h at 250 °C)	[m ² /g]	-	135
Pore volume (0 - 1,000 nm pore diameter)	[cm ³ /g]	-	0.23
Average pore radius	[nm]	-	3.2
Al ₂ O ₃ content	[%]	-	66
C content	[%]	3.8	6.5
Particle size (dynamic laser scattering)		d ₁₀ : 0.7 d ₅₀ : 2.2 d ₉₀ : 8.6	d ₁₀ : 0.3 d ₅₀ : 1.2 d ₉₀ : 8.5

Application as filed

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Table 3 Dispersibility of Disperal™ S / Marlon™ AS-3 In Various Solvents

Solvent	Dispersibility [%]	Particle Size (PCS) [nm]	Transmission [%]
Toluene	95.5	166	63.7
THF	99.0	113	32.3
Butanol	99.0	130	44.5
MTBE	85	-	6.8
Trichloromethane	98.5	64	42.3

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Table 4 Dispersibility of Disperal™ PTSA In Solvents Mixtures (10 wt% Solids)

Solvent	Ratio	Particle Size (PCS) [nm]	Centrifugation Stability (2,000 rpm/10 min) [%]
CHCl ₃ : MeOH	90 : 10	90	98
CHCl ₃ : MeOH	70 : 30	70	97
CHCl ₃ : MeOH	50 : 50	80	97.5
CHCl ₃ : MeOH	30 : 70	107	97.5
CHCl ₃ : MeOH	10 : 90	70	98.5
CH ₂ Cl ₂ : MeOH	90 : 10	97	98
CH ₂ Cl ₂ : MeOH	70 : 30	109	96
CH ₂ Cl ₂ : MeOH	50 : 50	103	96.3
CH ₂ Cl ₂ : MeOH	30 : 70	97	98.5
CHCl ₃ : Acetone	70 : 30	148	84
CHCl ₃ : Acetone	50 : 50	52	97.5

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ART 34 AMDT

Claims as amended in PCT Chapter II proceedings

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Claims

1. A process for preparing modified metal oxides or
5 metal aquoxides that are dispersible in organic
solvents characterised by the following steps
 - (I) by reaction of
 - (A) one or a plurality of metal oxide(s) or metal
10 aquoxide(s) having a crystallite size of 4 to
100 nm, determined by x-ray diffraction on the
021 reflex, and a particle size of 5 to 500 nm,
determined by photon correlation spectroscopy
in dispersion
- with
 - (B) one or a plurality of organic sulfonic acid(s),
15 where
 - (i) in case the reaction takes place in a
mainly aqueous medium or in the absence of
20 a diluent/solvent, the organic sulfonic
acid is a mono-, di-, or trialkylbenzene
sulfonic acid, wherein the alkyl resi-
due(s) are C₁ to C₆ alkyl residue(s) and
wherein the component (A), calculated as
25 metal oxide, and (B) are used at weight
ratios from 98:2 to 70:30, or
 - (ii) in case the reaction takes place in the
presence of an organic aprotic solvent or
an organic protic solvent, the organic
30 sulfonic acid comprises at least 14 carbon
atoms and at least one aromatic ring, and
wherein the components (A), calculated as
metal oxide, and (B) are used at weight
ratios from 98:2 to 70:30.

Claims as amended in PCT Chapter II proceedings

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- (II) drying the modified metal oxides or metal
5 aquoxides, and
(III) dispersing in organic solvents to get a
dispersion
2. The process of claim 1,
10 characterized in that as metal oxides or metal
aquoxides, such metal oxides or metal aquoxides
containing aluminium, preferably aluminas, alumina
hydrates, particularly preferred boehmitic or
pseudoboehmitic aluminas, aluminum silicate, or
15 Si/Al mixed oxides are employed.
3. A process according to any one of the preceding
claims,
characterized in that the organic sulfonic acid is
20 toluenesulfonic acid, preferably p-toluenesulfonic
acid.
4. A process according to claim 1 or 2,
characterized in that the organic sulfonic acid is
25 an organic compound of the R-SO₃H type, in which R
is an alkyl-substituted aromatic hydrocarbon residue
with 16 to 24 carbon atoms.
5. A process according to any one of the preceding
30 claims,
characterized in that the metal oxides or metal
aquoxides and the organic sulfonic acid are brought
into contact at temperatures from 0 to 140°C, pre-
ferably from 0 to less than 90°C.

Claims as amended in PCT Chapter II proceedings

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6. A process according to any one of the preceding
5 claims,
characterized in that the metal oxides or metal
aquoxides are brought into contact with the organic
sulfonic acid for a period from 30 seconds to 7
days, preferably from 30 to 90 minutes, and pre-
10 ferably with stirring.
7. A process according to any one of the preceding
claims,
characterized in that the modified metal oxides or
15 metal aquoxides are dried by spray drying, freeze
drying, microwave drying, drying in supercritical
solvents, filtration, contact drying, or rotary drum
drying.
- 20 8. A process according to any one of the preceding
claims,
characterized in that the modified metal oxides/
metal aquoxides are dispersible in organic solvent
as dispersions having a solid content of 10 to 35
25 wt%, preferably 20 to 30 wt%.
9. A process according to any one of the preceding
claims,
characterized in that the modified alumina hydrate
30 is processed into molded articles by extrusion, pel-
leting, or spherical drop forming processes.

Claims as amended in PCT Chapter II proceedings

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10. A process according to any one of the preceding claims,
5 characterized in that the metal oxides or metal aquoxides are taken up in an organic solvent and this solvent is exchanged for a second solvent.
10. Metal oxide or metal aquioxide dispersion obtainable by the use of a dispersant and a metal oxide or metal aquioxide according to any one of the preceding claims, wherein the dispersant
15 - a aprotic polar organic solvents,
- a protic, polar organic solvents having at least two carbon atoms, and/or
- a apolar organic solvents.
12. Metal oxide or metal aquioxide dispersion of claim 11,
20 characterized in that the dispersion contains an additive of at least one organic polymeric/oligomeric viscosity-adjusting agent, preferably cellulose, a cellulose derivative, a poly-acrylate, or a polyvinyl alcohol.
- 25 13. Metal oxide or metal aquioxide dispersion of claim 11,
30 characterized in that the dispersant is a solvent-based paint or lacquer or a water-insoluble plastics.

Claims as amended in PCT Chapter II proceedings

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14. Use of the metal oxides or metal aquoxides
5 dispersions of claim 11 for preparing coatings,
preferably transparent coatings on foils,
metals/metal oxides, glass, PVC, and other plastics.
15. Use of the metal oxides or metal aquoxides
10 dispersions of claim 11 for the production of
catalyst carrier.

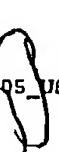
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D-99005 UE+CA


Abstract as filed

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Abstract

- 5 The present invention relates to a process for preparing metal oxides or metal aquoxides, especially alumina hydrates which can be dispersed in organic solvents, and to sulfonic acid-modified metal oxides or metal aquoxides that can be prepared by this process.

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D-99005 US+CA

Title: Process for the Preparation of Metal
Oxides that are Dispersible in Organic Solvents

Inventors: Frank Michael Bohnen, et al.

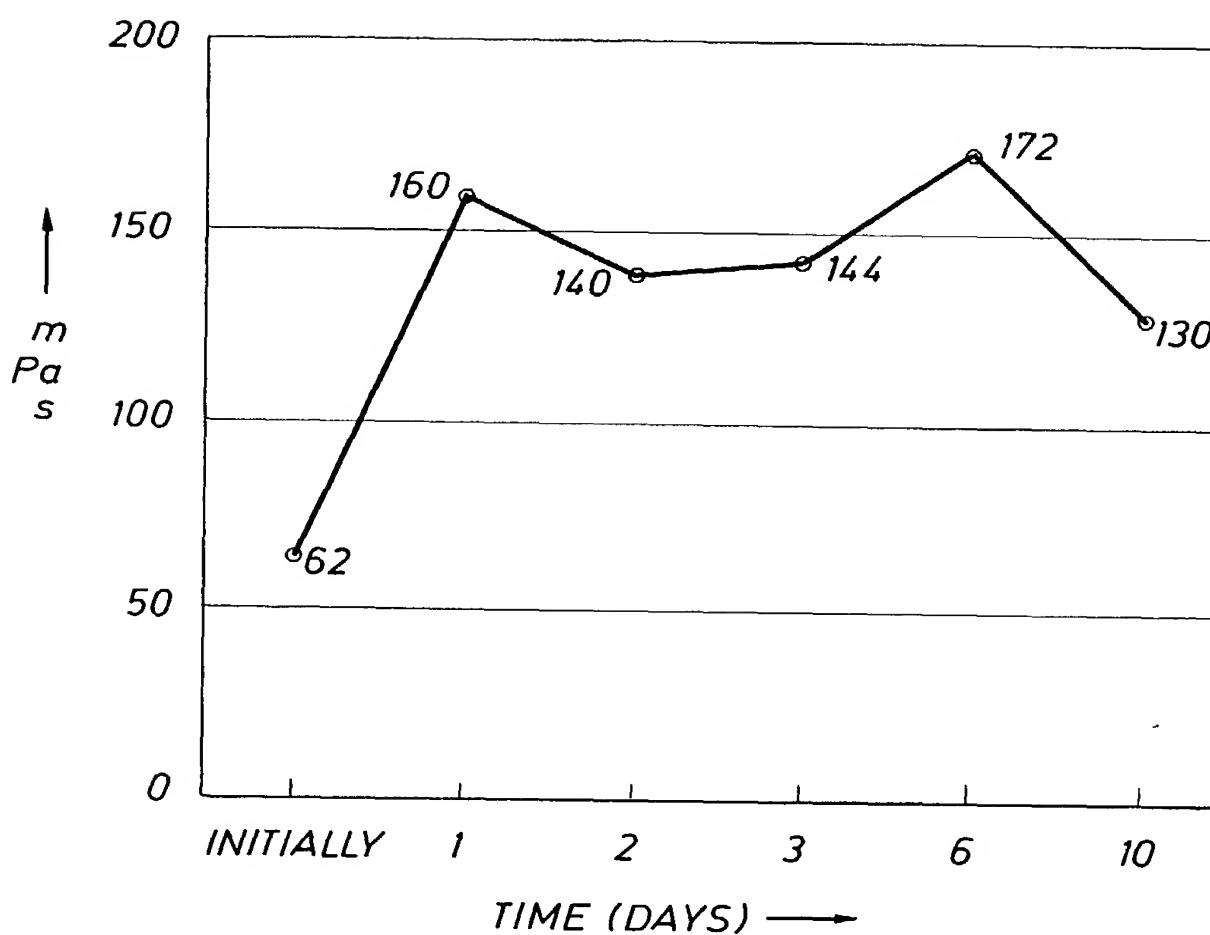
U.S.S N.: To Be Assigned

Atty: Docket No.: Muller-40

Contact: C James Bushman, 713-266-5593

1.0/030066

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Docket No.
Mueller-40

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
Method for Producing Metal Oxides Dispersibles in Organic Solvents

the specification of which

(check one)

is attached hereto.

was filed on January 3, 2002

as United States Application No. or PCT International

Application Number 10/030,066

and was amended on

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

19931204.4

Germany

7 July 1999

□

(Number)

(Country)

(Day/Month/Year Filed

(Nyushka)

(Country)

(Day/Month/Year Filed)

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/DE00/02163

6 July 2000

Pending

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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